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Andrew L. Cooksy

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14. ABSTRACT
This project seeks to expand our understanding of the dynamics of combustion intermediates subject to relocalization by a combination of gas-phase laboratory spectroscopy, photochemical studies, and ab initio computations. (1) Spectroscopy. Survey scans between 1800 and 2000 cm-1 of an acetylene/CO discharge, both at room temperature and at 110 K, reveal rich spectra. Students are currently working to assign the lines. Gaps in earlier scans are being filled by means of a new quantum cascade laser. Our apparatus generates stimulated emission in ozone at a previously undetected 5 micron region, but work remains to characterize the relevant

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Andrew Cooksy
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Report Title

Final Report: Chemical Studies of Free Radical Relocalization

ABSTRACT

This project seeks to expand our understanding of the dynamics of combustion intermediates subject to relocalization by a combination of gas-phase laboratory spectroscopy, photochemical studies, and ab initio computations. (1) Spectroscopy. Survey scans between 1800 and 2000 cm-1 of an acetylene/CO discharge, both at room temperature and at 110 K, reveal rich spectra. Students are currently working to assign the lines. Gaps in earlier scans are being filled by means of a new quantum cascade laser. Our apparatus generates stimulated emission in ozone at a previously undetected 5 micron region, but work remains to characterize the relevant dynamics. (2) Photochemistry. Students synthesized an acroleinyl radical precursor (2-bromopropen-3-al), but photochemical studies revealed no interesting chemistry. Studies are continuing, this time starting from commercially available acryloyl chloride (3-chloropropen-3-al). (3) Computations. We developed an optimized interpolation scheme for use with FEMvib, our solver for the vibrational Schrodinger equation on arbitrary potential energy surfaces. This advance greatly expands the usefulness of this resource, which is now available as a public web service (http://islands.sdsu.edu). We completed studies of the propynonyl radicals, now in preparation for publication. New studies of the vibrational manifolds of cyclooctatetraenyl radical and selected hydrogen-transfer pathways in organotransition metal catalysis are underway.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/09/2015	7.00	Laurie A. Clare, An T. Pham, Francine Magdaleno, Jaqueline Acosta, Jessica E. Woods, Andrew L. Cooksy, Diane K. Smith. Electrochemical Evidence for Intermolecular Proton-Coupled Electron Transfer through a Hydrogen Bond Complex in a, Journal of the American Chemical Society, (12 2013): 0. doi: 10.1021/ja410061x
01/09/2015	10.00	Christophe Desmarets, Geoffrey Gontard, Andrew L. Cooksy, Marie Noelle Rager, Hani Amouri. Encapsulation of a Metal Complex within a Self-Assembled Nanocage: Synergy Effects, Molecular Structures, and Density Functional Theory Calculations, Inorganic Chemistry, (05 2014): 0. doi: 10.1021/ic402539x
01/09/2015	9.00	Aurélie Damas, Lise-Marie Chamoreau, Andrew L. Cooksy, Anny Jutand, Hani Amouri. ?-Bonded Dithiolene Complexes: Synthesis, Molecular Structures, Electrochemical Behavior, and Density Functional Theory Calculations, Inorganic Chemistry, (02 2013): 0. doi: 10.1021/ic302128q
01/09/2015	8.00	Salome Bhagan, David C. Marelius, David J. Charboneau, Kristine M. Schroeder, Jayneil M. Kamdar, Amanda R. McGettigan, Benjamin J. Freeman, Curtis E. Moore, Arnold L. Rheingold, Andrew L. Cooksy, Diane K. Smith, Jared J. Paul, Elizabeth T. Papish, Douglas B. Grotjahn. How Do Proximal Hydroxy or Methoxy Groups on the Bidentate Ligand Affect [(2,2?;6?,2"-Terpyridine)Ru(N,N)X] Water-Oxidation Catalysts? Synthesis, Characterization, and Reactivity at Acidic and Near-Neutral pH, European Journal of Inorganic Chemistry, (02 2014): 0. doi: 10.1002/ejic.201300826
08/31/2012	3.00	Julien Dubarle-Offner, M. Rosa Axet, Lise Marie Chamoreau, Hani Amouri, Andrew L. Cooksy. Enantiomerically Pure, Planar Chiral Cp*Ru Complexes: Synthesis, Molecular Structures, DFT and Coordination Properties, Organometallics, (06 2012): 0. doi: 10.1021/om300210c
08/31/2012	4.00	Peter Kovacic, Andrew Cooksy. Novel, unifying mechanism for amphotericin B and other polyene drugs: electron affinity, radicals, electron transfer, autoxidation, toxicity, and antifungal action., MedChemComm, (01 2012): 274. doi: 10.1039/c2md00267a
TOTAL:	**6**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Vibrational energies and wavefunctions on a 3D tonal, coupled cluster isomerization potential energy surface of cyclooctatetraenyl radical
Gerardo Soriano, Peter Zajac, Andrew L. Cooksy
National Meeting of the American Chemical Society, San Francisco CA, August 10-14 2014.

2. Explicit vibrational analysis of the alkyne-vinylidene isomerization on a heterocyclic ruthenium catalyst
Babgen Manookian, Vy Le, Gerardo Soriano, Douglas B. Grotjahn, Andrew L. Cooksy
National Meeting of the American Chemical Society, San Francisco CA, August 10-14 2014.

3. VIBRATIONAL ANALYSIS OF HYDROGEN ATOM DYNAMICS IN THE PRESENCE OF A HETEROCYCLIC ORGANOMETALLIC CATALYST
Vy Le, Babgen Manookian, Gerardo Soriano, Douglas B. Grotjahn, Andrew L. Cooksy
National Meeting of the American Chemical Society, San Francisco CA, August 10-14 2014.

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
11/04/2011	1.00 Andrew L. Cooksy, Dong Xu, Peter Zajac. RELOCALIZATION DYNAMICS ON POTENTIAL ENERGY SURFACES OF COMBUSTION-RELATED FREE RADICALS, Army Science Conference. 29-NOV-10, . : ,
TOTAL:	**1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper
01/09/2015	5.00 Jernej Stare, Dong Xu, Andrew Cooksy, Peter Zajac. Relocalization Dynamics of the HC3O Free Radical by Finite Element Method Vibrational Analysis, J. Chem. Phys. (01 2015)
01/09/2015	11.00 Andrew L. Cooksy, C. A. Gottlieb, T. C. Killian, P. Thaddeus, Nimesh Patel, Ken H. Young, M. C. McCarthy. Vibrationally Excited C4H, Astrophysical Journal (09 2014)
11/04/2011	2.00 Peter Zajac, Andrew L. Cooksy, Mohammad Abouali, Ali Nadim. COMPARISON OF INTERPOLATION METHODS ON PROPYNONYL RADICAL POTENTIAL ENERGY SURFACE, J Computational Chemistry (11 2011)
TOTAL:	**3**

Number of Manuscripts:

Books

Received	Book
TOTAL:	

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Scott Burley	0.05	
Lee Wang	0.05	
Peter Zajac	0.00	
FTE Equivalent:	**0.10**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Erich Wolf	1.00
Nuradhika Herath	1.00
FTE Equivalent:	**2.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Andrew Cooksy	0.00	
B. Mikael Bergdahl	0.06	
FTE Equivalent:	**0.06**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Stuart Mayberry	0.20	Chemistry
Michael Baude	0.30	Chemistry
Babgen Manookian	0.15	Chemistry
Vy Le	0.15	Chemistry
Jane Lucas	0.15	Chemistry
Alita Ghanim	0.05	Chemistry
FTE Equivalent:	**1.00**	
Total Number:	**6**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....

Names of Personnel receiving masters degrees

NAME	
Scott Burley (Bergdahl student)	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Peter Zajac	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Chemical Studies of Free Radical Relocalization

Andrew L. Cooksy
San Diego State University
Department of Chemistry and Biochemistry

Abstract

This project seeks to expand our understanding of the dynamics of combustion intermediates subject to relocalization by a combination of gas-phase laboratory spectroscopy, photochemical studies, and ab initio computations. (1) Spectroscopy. Survey scans between 1800 and 2000 cm^{-1} of an acetylene/CO discharge, both at room temperature and at 110 K, reveal rich spectra. Students are currently working to assign the lines. Gaps in earlier scans are being filled by means of a new quantum cascade laser. Our apparatus generates stimulated emission in ozone at a previously undetected 5 micron region, but work remains to characterize the relevant dynamics. (2) Photochemistry. Students synthesized an acroleinyl radical precursor (2-bromopropen-3-al), but photochemical studies revealed no interesting chemistry. Studies are continuing, this time starting from commercially available acryloyl chloride (3-chloropropen-3-al). (3) Computations. We developed an optimized interpolation scheme for use with FEMvib, our solver for the vibrational Schrodinger equation on arbitrary potential energy surfaces. This advance greatly expands the usefulness of this resource, which is now available as a public web service (http://islands.sdsu.edu). We completed studies of the propynonyl radicals, now in preparation for publication. New studies of the vibrational manifolds of cyclooctatetraenyl radical and selected hydrogen-transfer pathways in organotransition metal catalysis are underway.

Summary of important results:

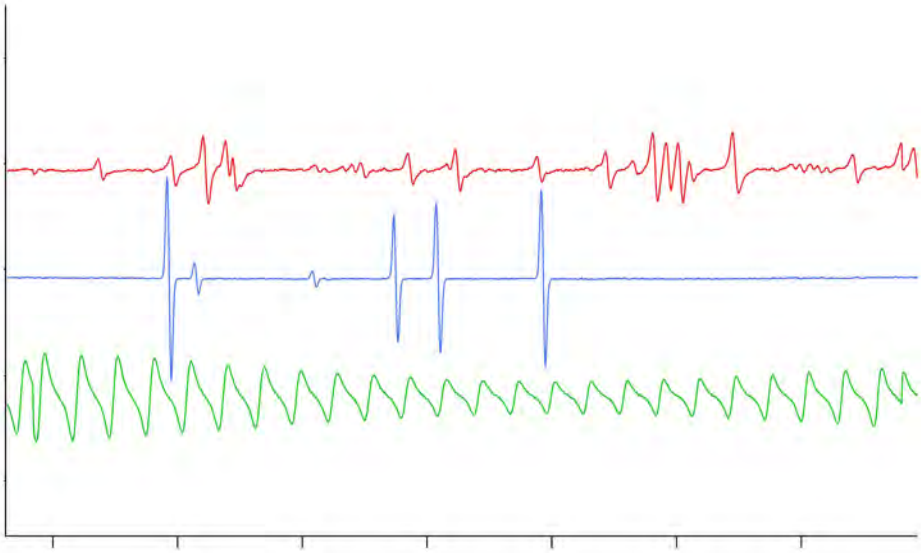
I. Laboratory Spectroscopy of Gas-phase Hydrocarbon Radicals.

We have carried out line surveys in a He/CO/HCCH electric discharge over the roughly 1800–2000 cm^{-1} region at high resolution. Surveys were carried out both at 100 K (using liquid nitrogen cooling) and at room temperature, where we expect to see a greater abundance of small (< 3 carbon) molecules. We have added a new quantum cascade laser (QCL) from Daylight Solutions to the system, which will enable us to scan without mode hops from 1840 to 1950 cm^{-1}.

From these high-resolution spectra, we have now observed and calibrated roughly 200 transitions, in addition to those assigned to the ethynyl radical, (Fig. 1). These appear to be too sparse and strong to be HCCCO, but are likely to be an as-yet unidentified band of one of the other ketenyl-like radicals, since they require presence of CO. Assignment of the transitions observed is being carried out using transition frequencies and

molecular constants in the literature archive and NIST databases. We have also adapted the PI's program for fitting high resolution rotational data in order to predict the rovibrational spectra of the target radicals. Undergraduate students have participated in the project by finding suitable estimates for the distortion and vibration-rotation coupling constants and simulating the spectra for comparison to the experimental measurements. We continue to scan under different chemistry (using butadiene as a precursor, omitting the CO) while assigning the archived spectra.

Figure 1: Scan near 2020cm^{-1} showing unidentified spectra (center trace, blue) under the same sample conditions in which CCH is observed. This spectrum also shows the reference gas (top, red) and etalon fringes (bottom, green) used to calibrate the frequencies.



The development of the spectrometer and much of the scanning were carried out during the funding period by former postdocs Nuradhika Herath (now at Oak Ridge National Laboratory) and Erich Wolf (Oregon State U.), and former undergraduate student Michael Baudé (now a graduate student at U. Tennessee), all of whom were supported by this grant. Nearly twenty other undergraduates have worked on this experiment to varying degrees for course credit and in some cases for summer pay.

II. Photochemical Studies of Related Radicals in Solution.

We have synthesized bromo-cyclooctatetraene, 2-bromoacrolein, and chloroprene, to serve as precursors in the formation of cyclooctatetraenyl (c-C8H7), acroleinyl, and butadienyl radicals, respectively. However, the bromo-cyclooctatetraene has proven too difficult to keep stable for those experiments to have yet been carried out. The other samples have been photolyzed by a Continuum Surelite-II YAG laser operating at a

frequency-quadrupled 266 nm. The samples are analyzed before and after photolysis by means of NMR, IR, and UV/vis spectra, with and without the co-dissolved radical quencher CH_3I. The precursor synthesis has been carried out by Prof. Mikael Bergdahl and graduate students Lee Wang and Scott Burley, all of whom have received partial support from this grant.

A series of tests on 2-bromoacrolein yielded disappointing results, as the sample appears to form acrolein in the presence of CH_3I, rather than any of its isomers. This compound, while the first to be prepared, was also the least promising with regards to these studies, because the relocalization isomer that would be formed (a dienal) is predicted to be less stable than the parent radical. In contrast, the radical formed from chloroprene should spontaneously deform from the 1,3-diene to the allylic 1,2-dien-3-yl. We have also been investigating the analogous reaction involving acroleinyl radical by starting from acryloyl chloride, although this too is complicated by the delicate stability of the precursor compound. Those studies are experimentally more challenging, because the analytical spectra are more complex and the solvation and photolytic properties are less propitious, but we anticipate overcoming those difficulties in the upcoming experiments.

III. Computational Studies to Guide Both Sets of Experiments.

FEMvib, our program to solve the vibrational Schrödinger equation on an arbitrary potential energy surface, now allows the treatment of periodic coordinates such as internal rotations. This allowed us to participate in an ongoing study by the William Green group at MIT on suitable approximation methods for treating internal rotors in computational studies of combustion chemistry. The goal of the project is to find what approximation methods afford the best balance between accuracy and computational efficiency when estimating partition functions (and the associated thermodynamic properties) for molecules where hindered rotations are a substantial contributor to the dynamics. In this work, FEMvib provides a gold-standard, because we solve explicitly for all of the vibrational eigenstates of the system, allowing the partition function to be determined exactly within the limits of the potential energy surface provided. Calculations on a sample system are completed, and this manuscript will be submitted for publication this Fall.

Our analysis of the HCCCO system using FEMvib is complete and the manuscript being edited prior to submission. The preparation of this manuscript has been delayed by the need to carry out additional calculations of the partition functions, to better serve the combustion community. A high-quality three-dimensional potential energy surface has also been assembled for the acroleinyl radical, and analysis of the vibrational dynamics is forthcoming.

This work has been carried out entirely by graduate student Peter Zajac, who completed his doctoral research in Fall 2014.

Undergraduate Gerardo Soriano has been using FEMvib to analyze a new three-

diomensional potential energy surface for the C_8H_7 radical, and we expect to submit that paper this spring. Undergraduates Vy Le and Babgen Manookian have been testing a new application of FEMvib to organotransition metaql catalysts, capitalizing on a collaboration of our group with synthetic chemist Doug Grotjahn (also at SDSU). The driving concept is that the hydrogen transfer reactions catalyzed by his compounds may have suitably separated energy levels to allow a detailed quantum chemical analysis, which in turn may provide predictions of the kinetic isotope and other quantum effects at much greater than typical accuracy. This work is exploratory, but preliminary results suggest that it may be worthwhile.

New graduate students Pierre Winter and Richard LeCoultre are investigating the reaction surfaces of the target free radicals by coupled cluster calculations, and recent results indicate that the reaction C_4H_5 + C2H4 kinetically favors the 1,2-diene product over the thermodynamically more stable 1,3-diene, showing that the early transition states of these reactions may often cause the relocalization of these radicals to play a significant and unanticipated role in the combustion chemistry of unsaturated fuels. This is an avenue we now intend to investigate more thoroughly, examining the other radicals and combinations with other reactants.